中国科学院
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CO_2 Capture and Chemical Utilization

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Institute of Coal Chemistry
Chinese Academy of Science

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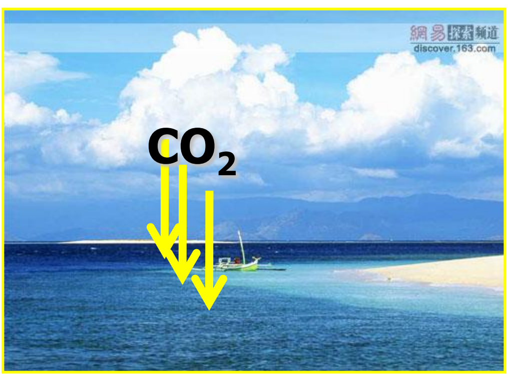
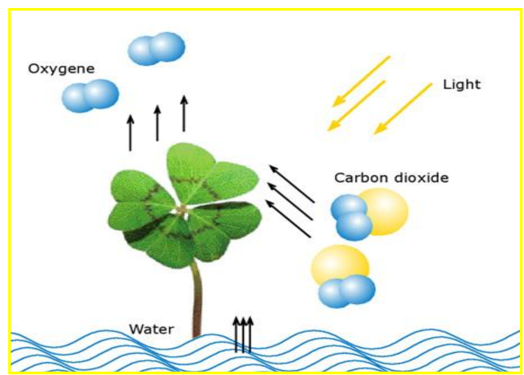
CO_2 and Climate Change

Carbon cycle: a positive CO_2 accumulation





24b tons of CO_2 were annually produced on the Earth as a result of human activity but CO_2 consume was limited

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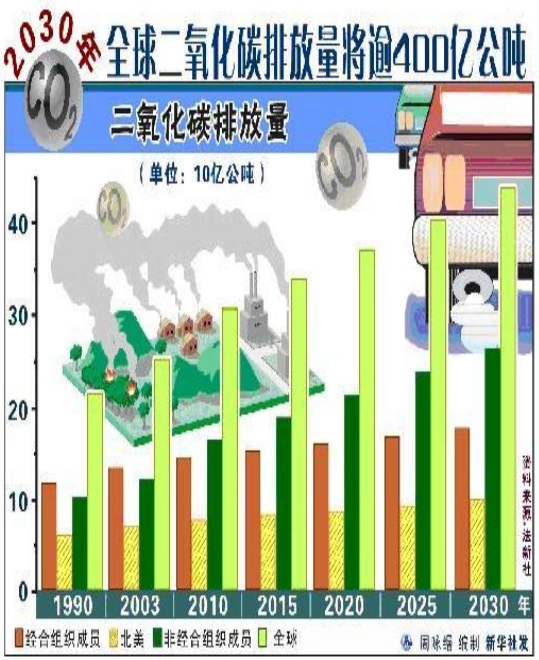
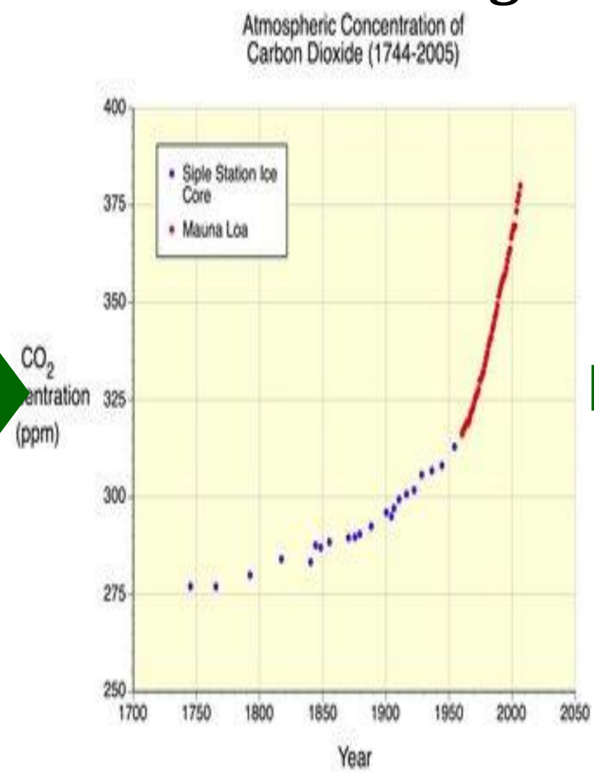
CO_2 and Climate Change

CO_2 accumulation and climate change

CO_2 concentration has increased rapidly from 1744 to 2005 and led to the climate change.





Glacier of Alps

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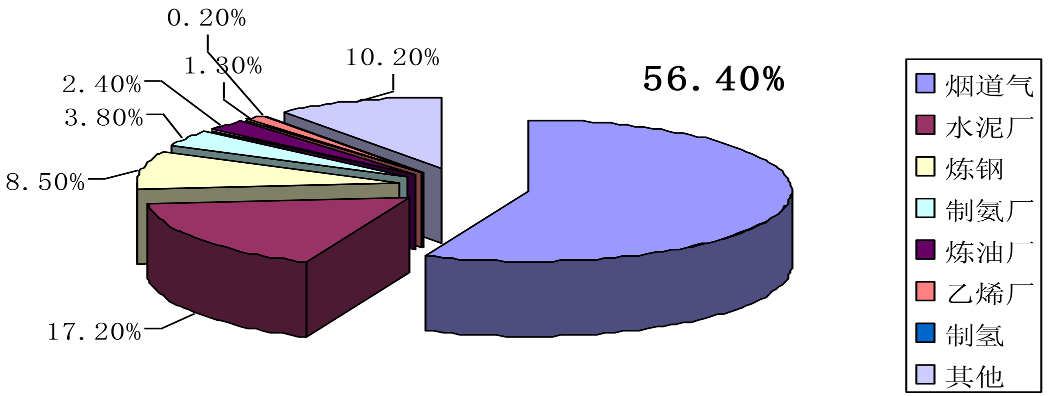
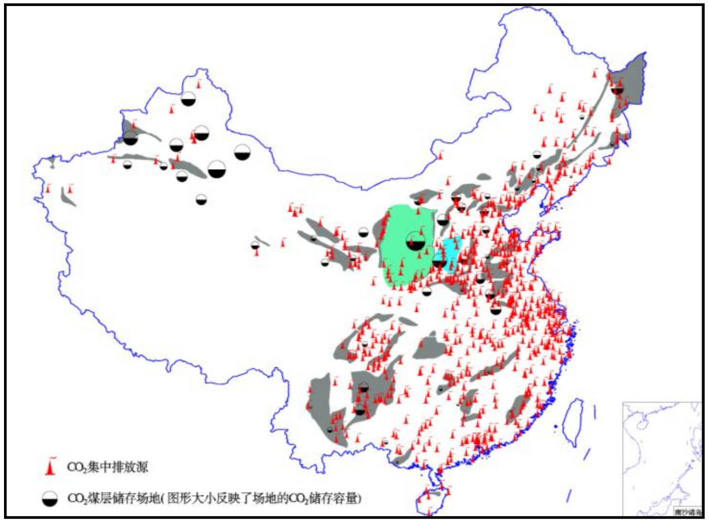
CO_2 and Climate Change

CO_2 emission and disribution



CO_2 point sources in China



60% of CO_2 emissions resulted from coal-fired plants. The CO_2 capture from large-volume and highly-concentrated CO_2 stationary source is technically feasible and cost-effective for sequestrating CO_2.

CO_2 and Climate Change

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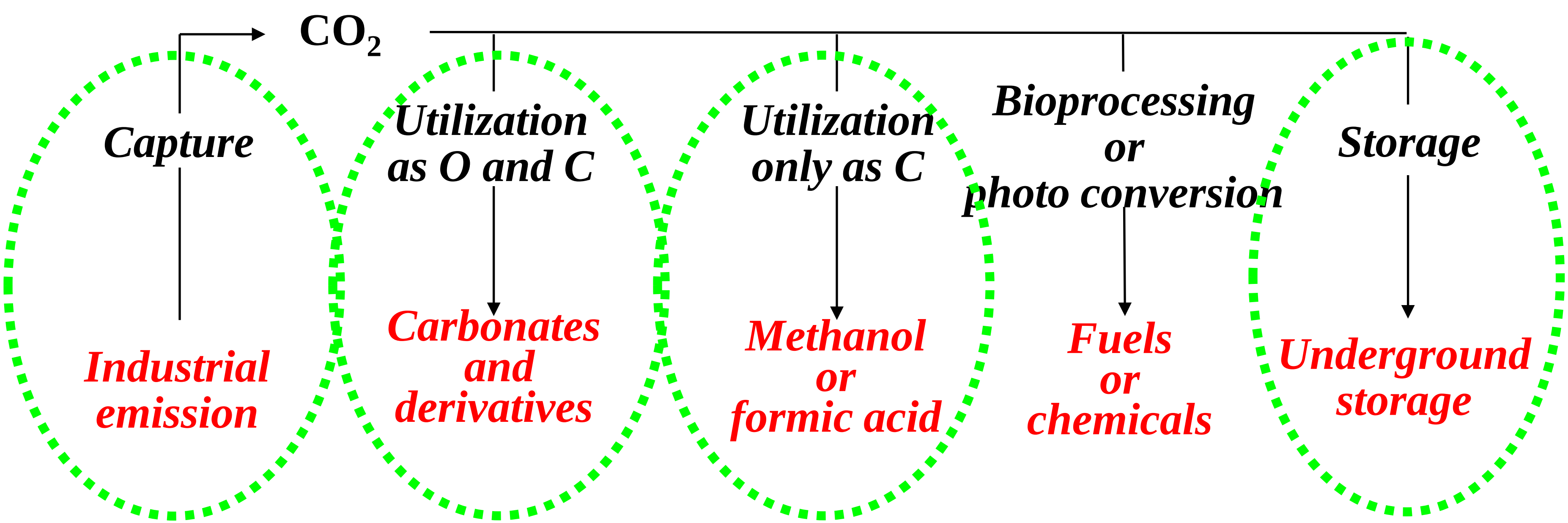
CO_2 capture, storage or utilization (CCSU)



Government and industries have recently paid much attention to CO_2 problem in China. MOST and NSFC initiate R&D program of abatement and CCSU .

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CO_2 Capture and Utilization

Present status of CO_2 capture

CO_2 capture at present

Absorption in aqueous amines

MEA、DEA、MDEA、DIPA、DGA etc.

Membrane processing

Polymer or inorganic oxide membranes.

Solid sorbents

activated carbon, amine-treated polymers, nanosized oxides.

These current technologies, when applied for CO_2 capture from coal-fired power plants, increase the electricity cost by more than 70%.

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CO_2 Capture and Utilization

Solution to cost reduction

The cost can be reduced if an effective CO_2 capture sorbent is developed which has

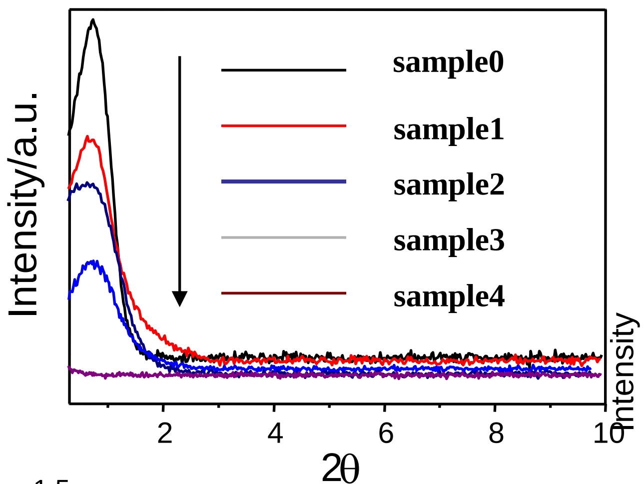
- **a high CO_2 adsorption capacity (>8% wt),**
- **a long-term regeneration capacity in a power plant flue gas environment(high-temperature, contaminants)**
- **a low energy requirement for regeneration compared to the large amount of energy required for the aqueous amine process.**

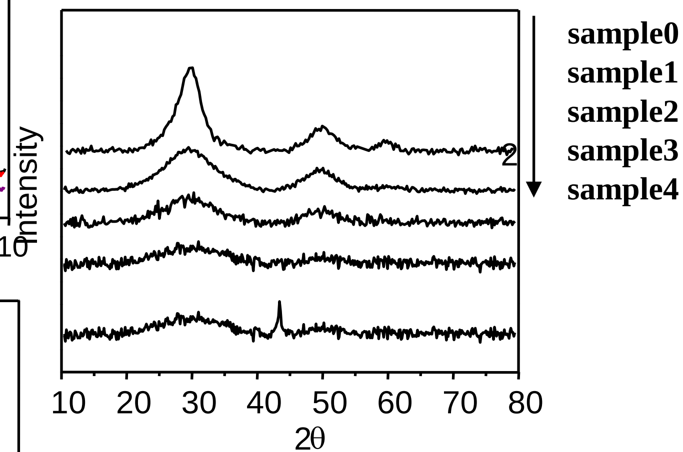
↓

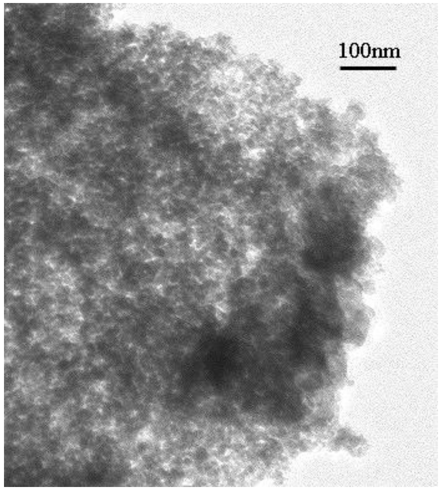
ICC focus on high-temperature CO_2 capture materials

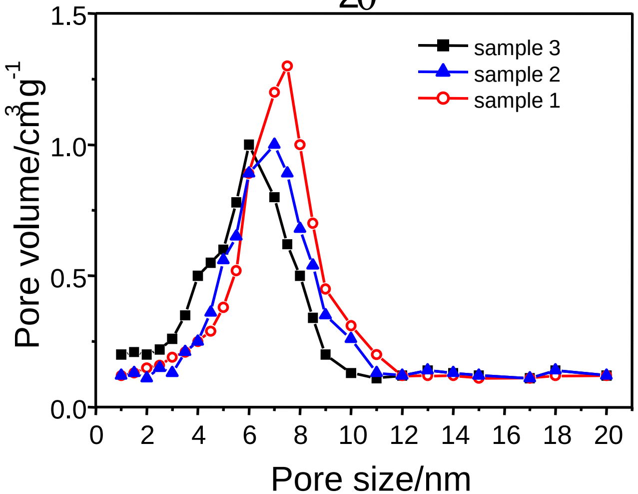
CO_2 Capture and Utilization

Materials for CO_2 capture at ICC









The focus is on the development of absorbents with the capture capacity over 10wt%.

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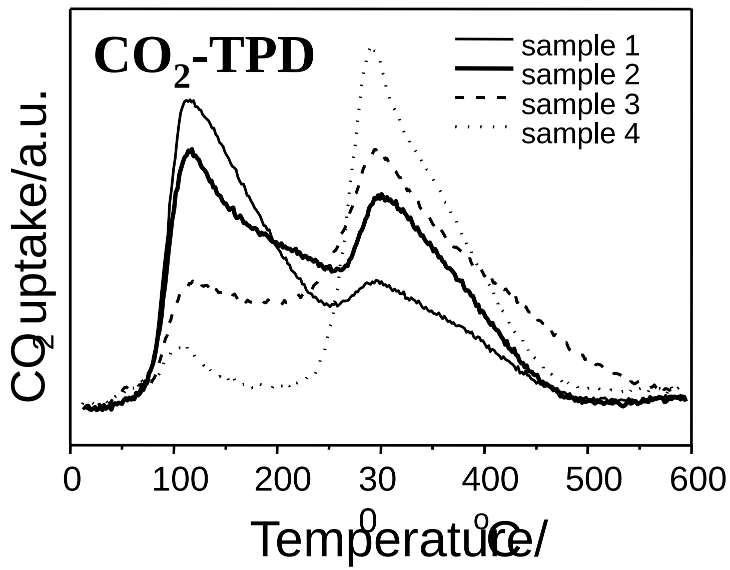
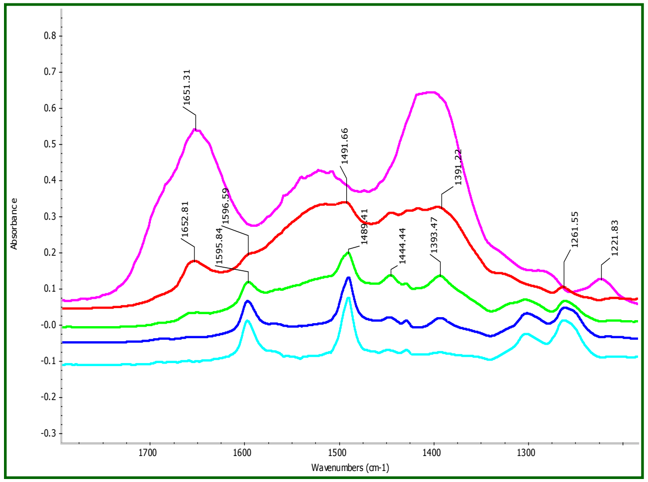
Materials for CO_2 capture at ICC





Solid soution of mesoporous with high stability showed both weak and strong of high basicity

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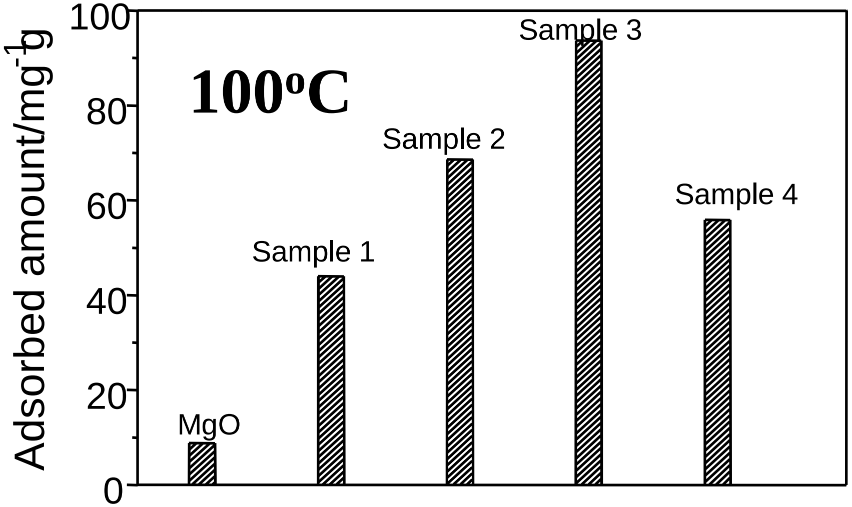
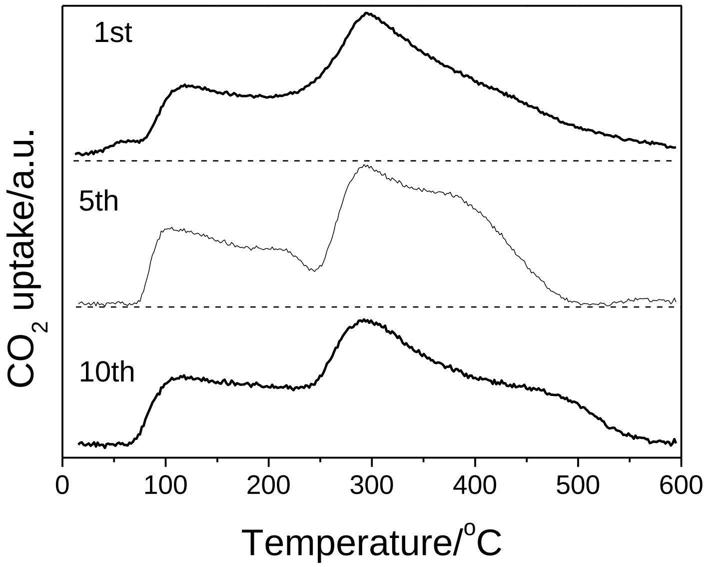
CO_2 Capture and Utilization

Materials for CO_2 capture at ICC

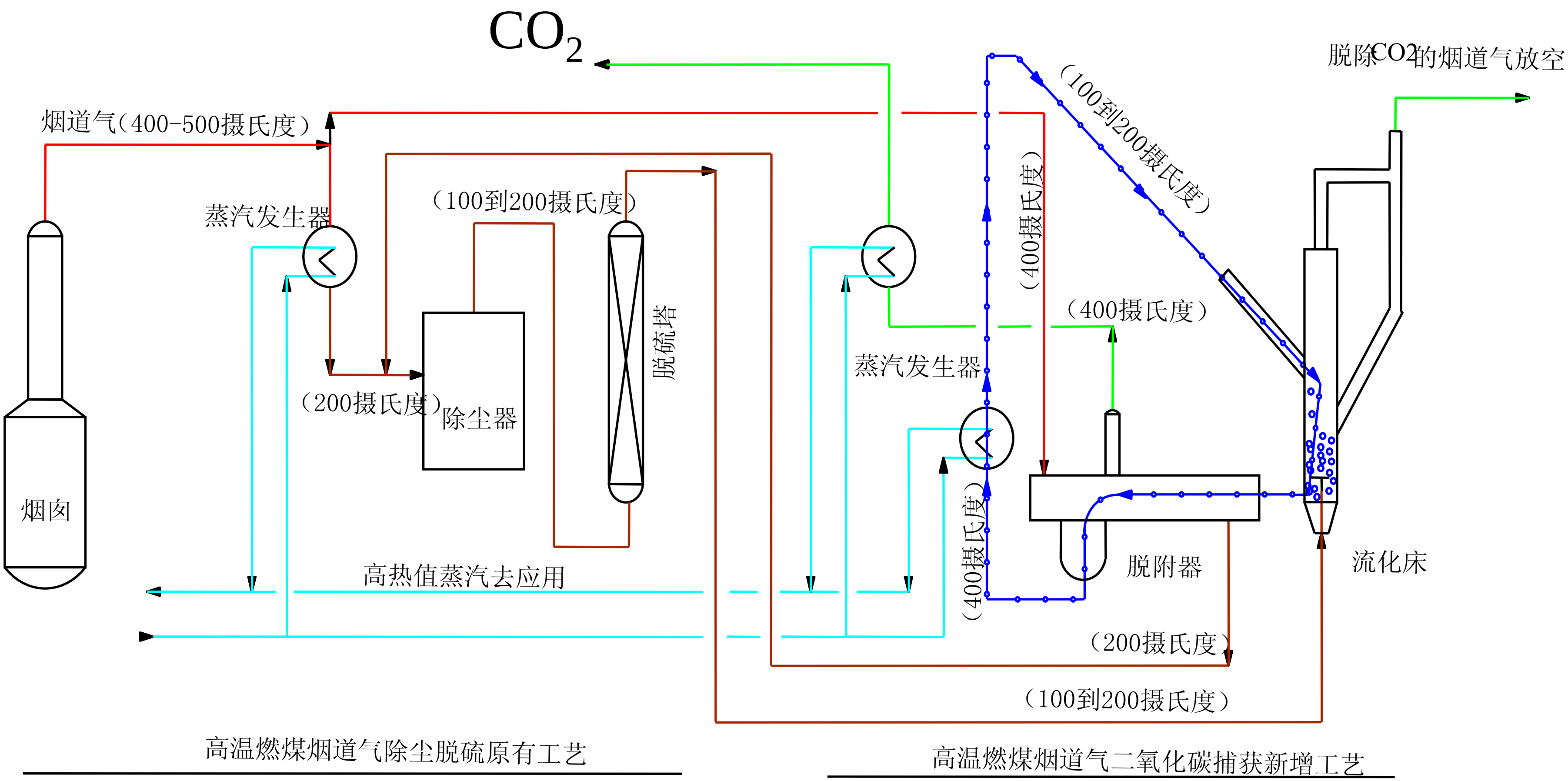




The material showed a fast uptake in 15min and then a high capacity of >10wt% at 100°C, and CO_2 TPD repeated well for sample 3 below 400°C, indicating a perfect reusability.

CO_2 Capture and Utilization

Technology development for CO_2 capture



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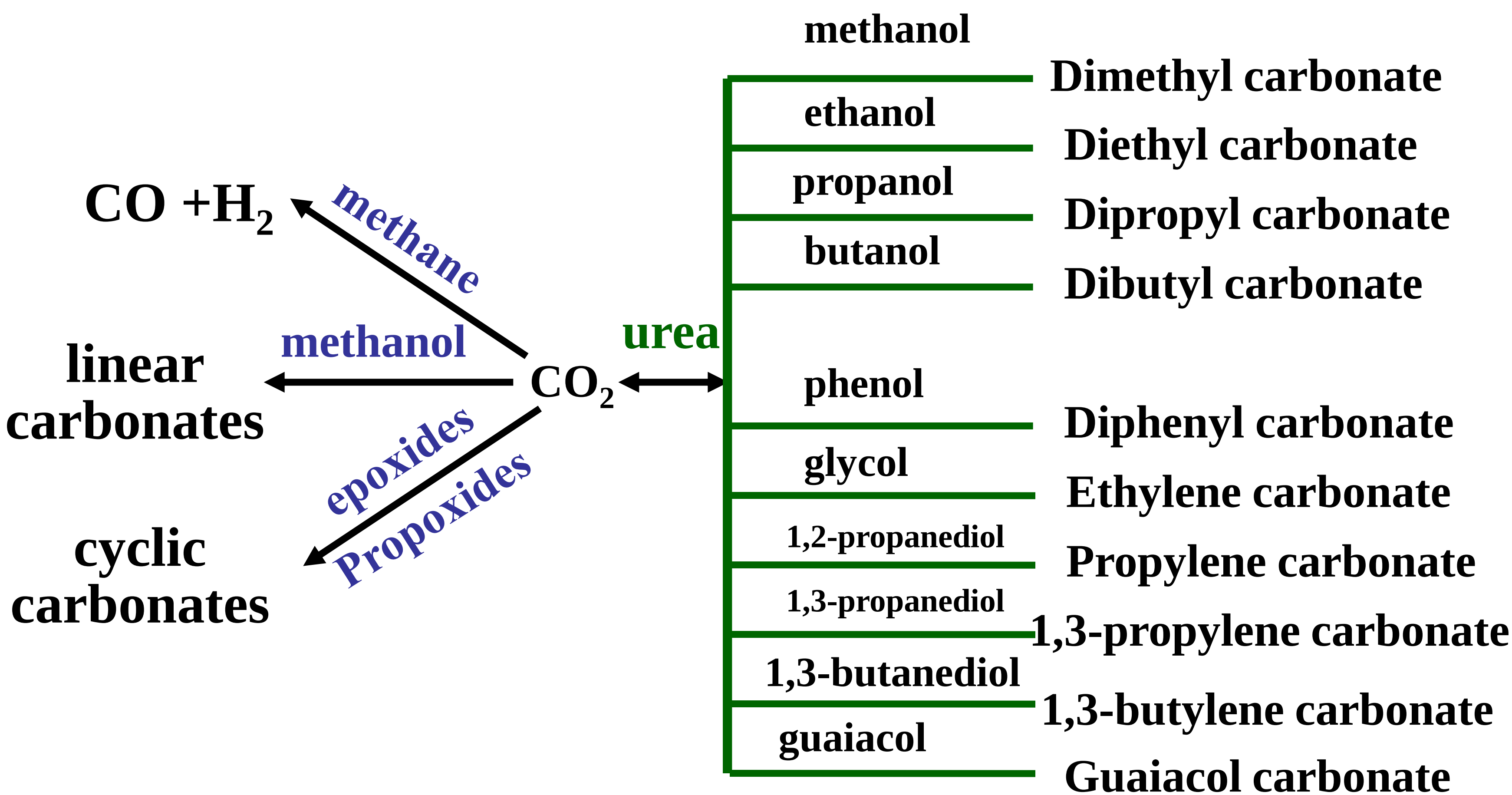
CO_2 Capture and Utilization

CO_2 chemical utilization at ICC



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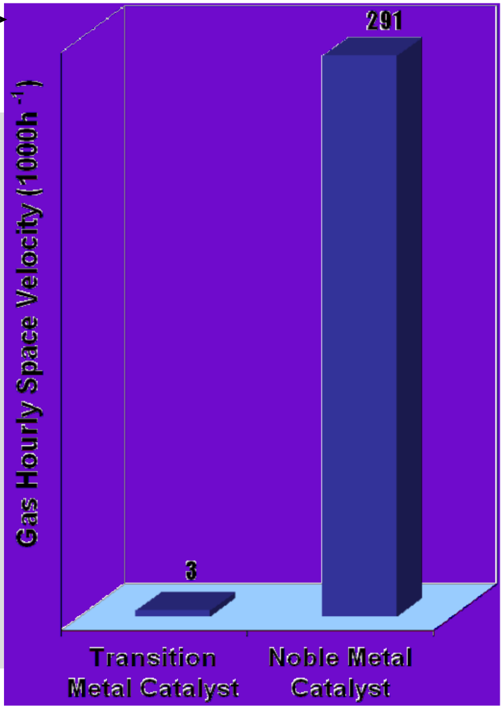
CO_2 Capture and Utilization

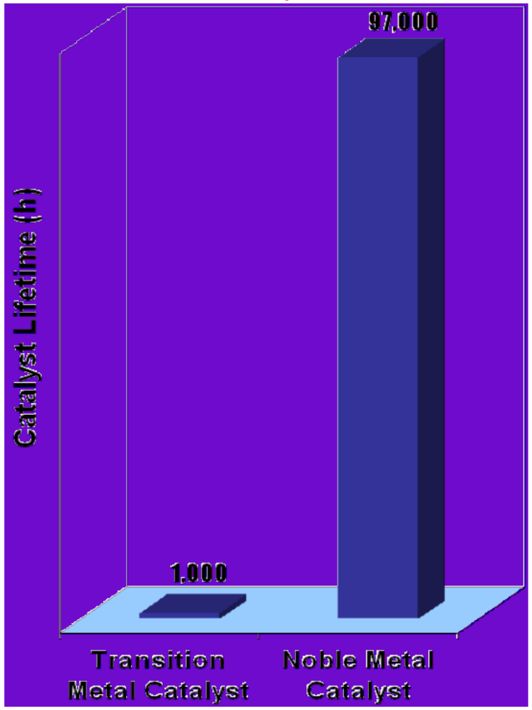
CO_2 reforming of methane

- ⊙ Rh is the most active metal, and has been well accepted for CPOX;
- ⊙ The barriers is to improve Ni catalyst activity and stability, especially to reduce carbon deposition.

Sensitivity Analysis

In order to have same syngas selling Price

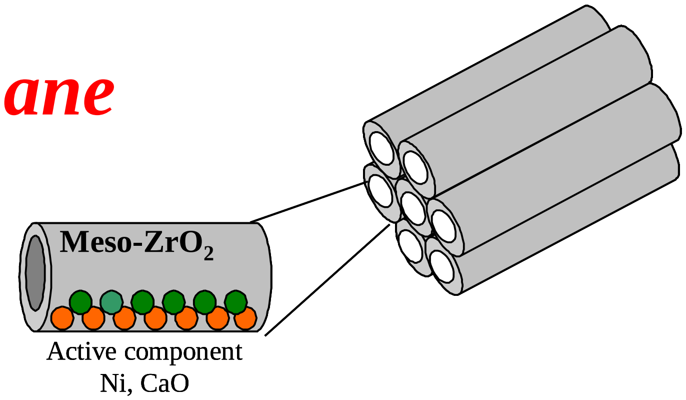




- ◆ 90% syngas yield with CH_4 to CO_2 molar ratio at 1:1 is assumed without dilution
- ◆ The noble catalyst charged for CDR is assumed to have price of \$1,000/kg
- ◆ Data by home-made EXCEL

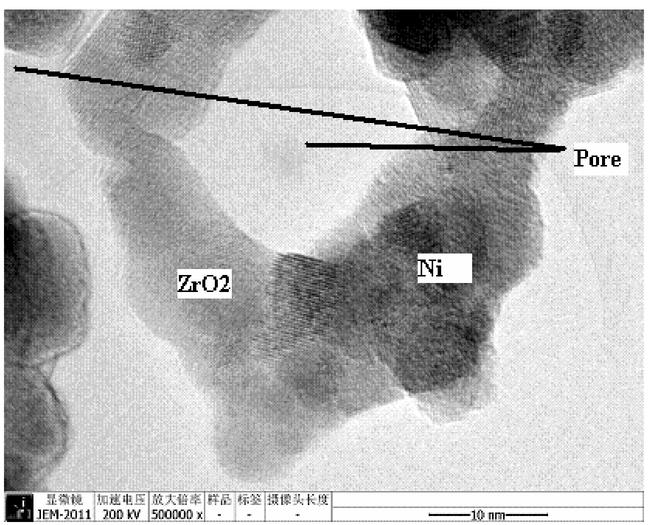
CO_2 Capture and Utilization

CO_2 reforming of methane



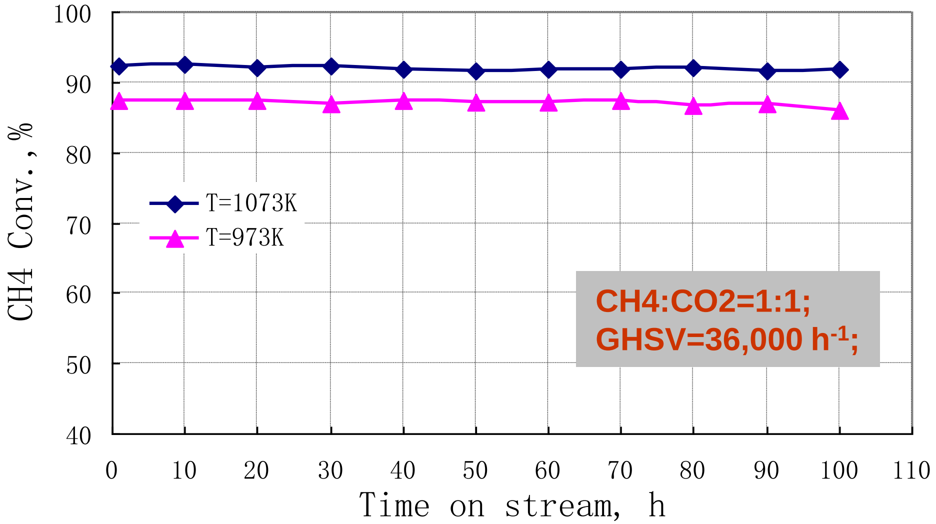
- **Mesoporous Nanocomposites**

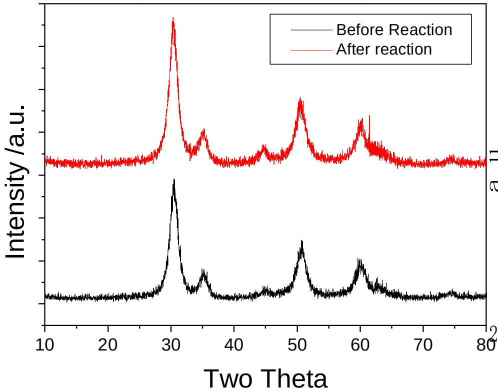
❖ Nano-particles with zero dimension take for no "steps" and "kinks"
❖ Carbon deposition occured only when the metal cluster is greater than a critical size
❖ Metals could be confined by meso-pores and hardly grow up
❖ Carbon deposition was favored by acidic supports, solid base could activate CO_2 and promote coke consumption.

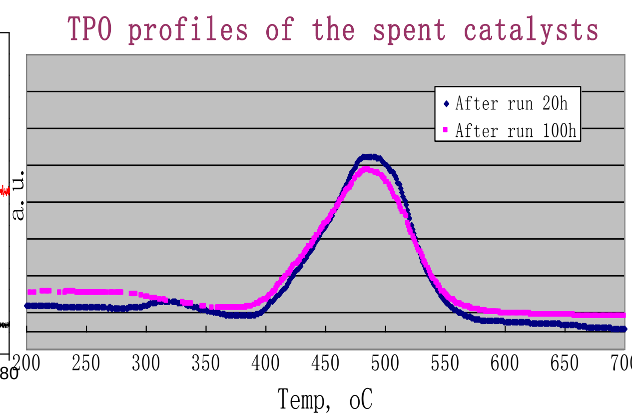


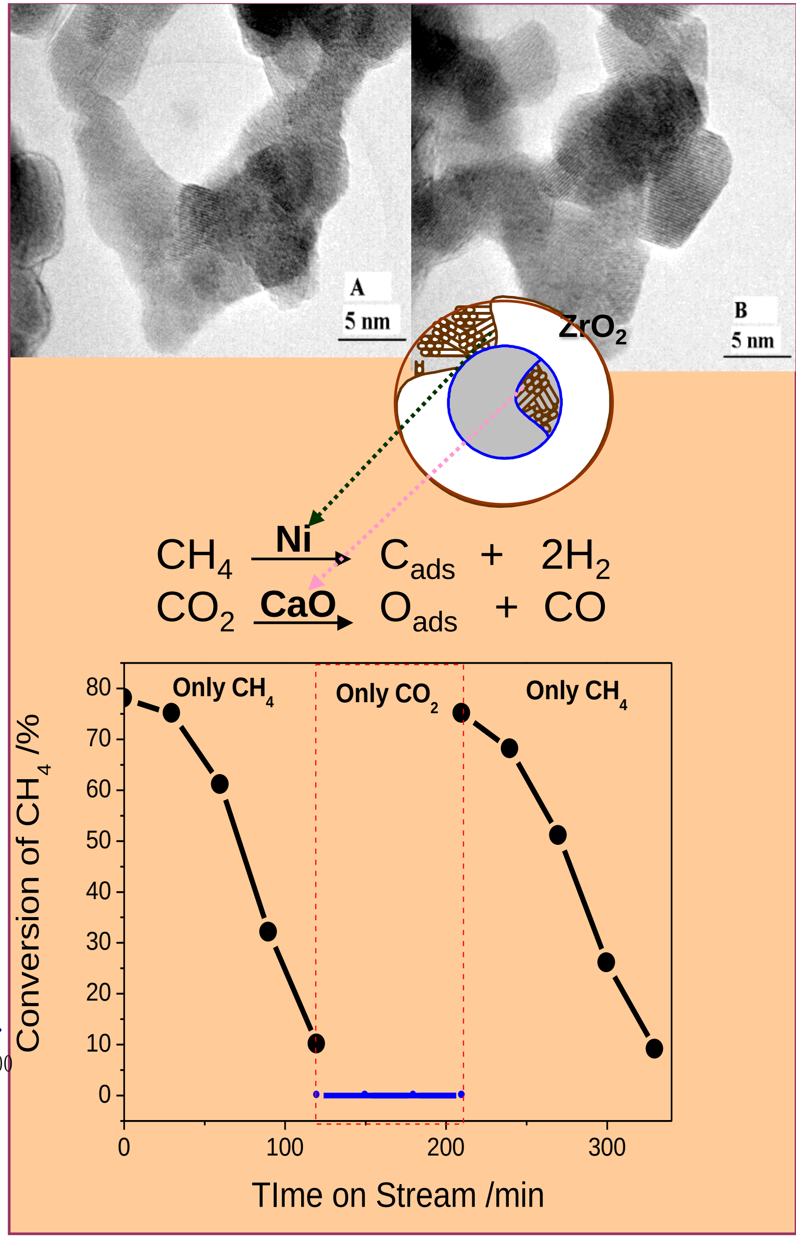
CO_2 Capture and Utilization

CO_2 reforming of methane





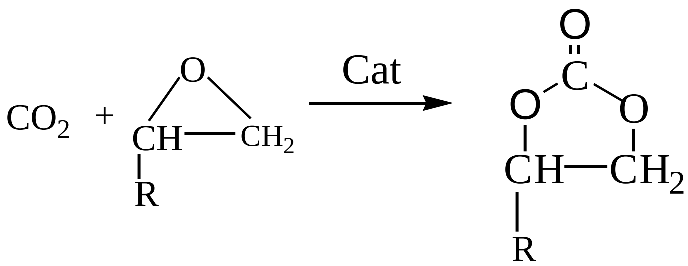


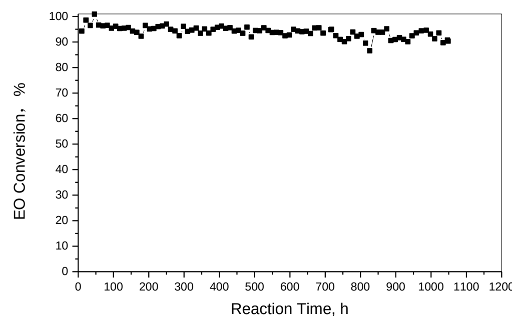


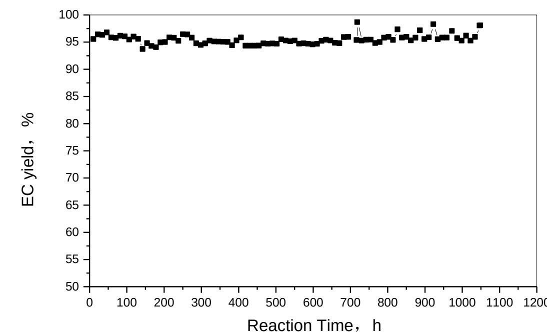
Highly Stable Ni-CaO-ZrO_2 Nanocomposites

CO_2 Capture and Utilization

CO_2 cycloaddition to propylene or ethylene carbonate





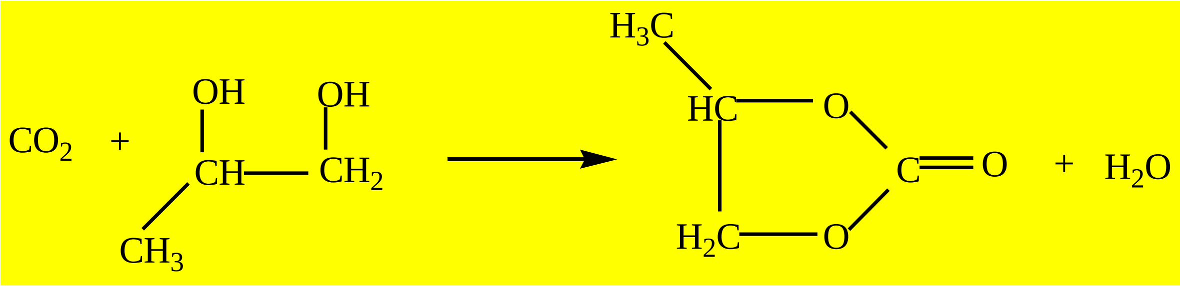


500t/a Pilot Plant

Both PO/EO conversion and PC/EC selectivity over heterogeneous catalysts approached to 100% at mild conditions. By a continual structural reactor, heat was successfully removed and then no deactivation was observed in 1000h operation in 500t/a Pilot Plant.

CO_2 Capture and Utilization

Cyclic carbonates from glycols in sc-CO_2



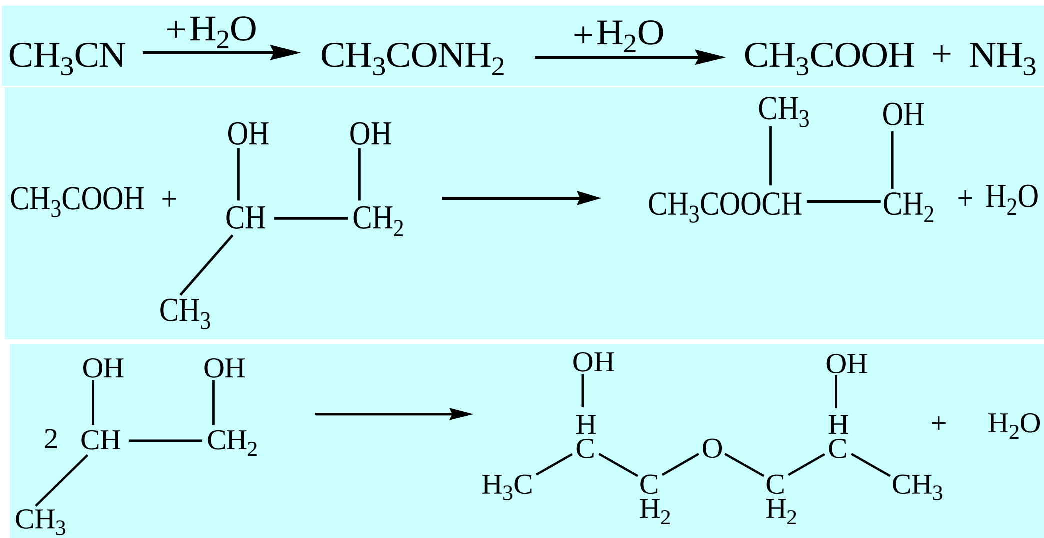
Problems:_
- **How to shift the equilibrium**
- **How to remove produced H_2O**

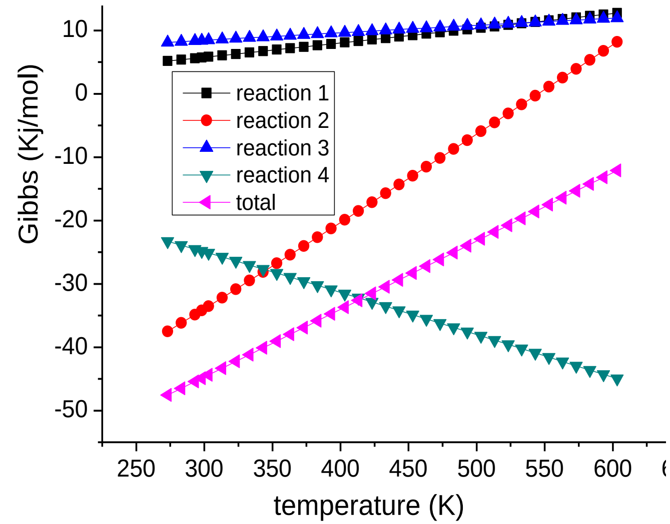
Strategies:_
- **Reaction take place in sc-CO_2**
- **CH_3CN as a coupling solvent**

CO_2 Capture and Utilization

Cyclic carbonates from glycols in sc-CO_2

Side reactions and thermodynamics





The by-product was mainly propylene glycol-2-acetate due to the hydrolysis of CH_3CN into acetamide and then acetic acid and ammonia (along with a small amount of dipropyleneglycol as expectable by-products).

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CO_2 Capture and Utilization

Cyclic carbonates from glycols in sc-CO_2

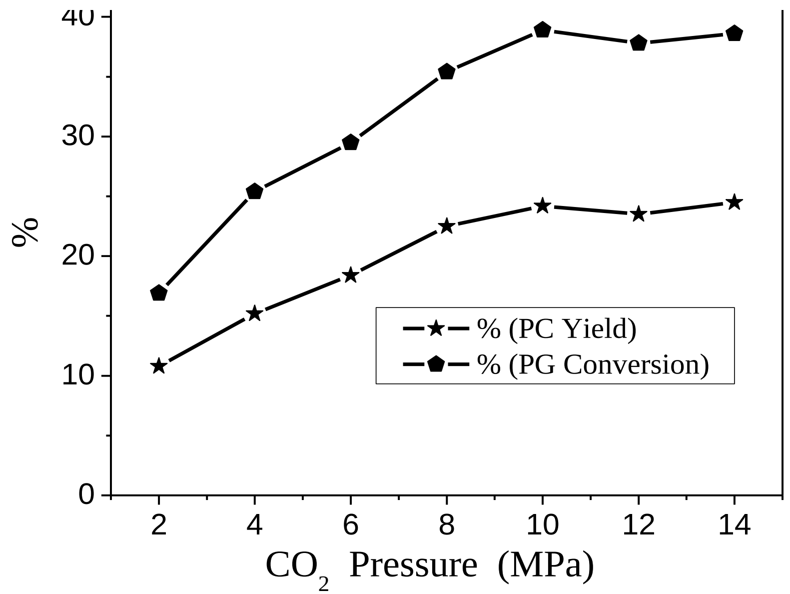
Catalyst	PG conversion %	Selectivity %		
		PC	PG-2-acetate	DPG
$FeCl_3$	42.5	62.3	36.5	1.2
$FeCl_3$ $6H_2O$	35.8	60.2	38.8	1.0
$FeCl_2$	38.9	60.4	38.2	1.4
$FeCl_2$ $4H_2O$	30.6	58.5	40.0	1.5
$CuCl_2$	15.6	57.7	41.5	0.8
$ZnCl_2$	39.2	45.6	37.4	17.0
$CoCl_2$	17.6	55.7	43.2	1.1
$NiCl_2$	14.5	56.6	42.4	1.0

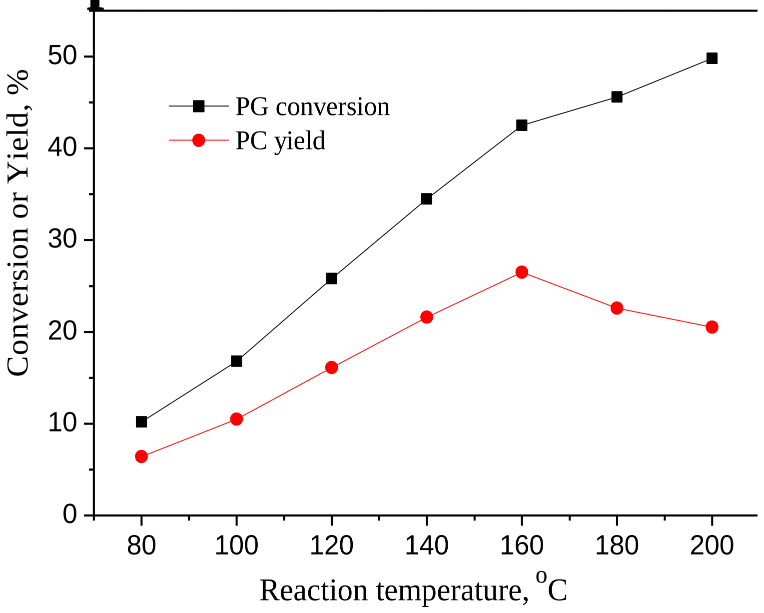
Fe halides appeared to be active towards the reaction of PG with sc-CO_2 but crystal water had the negative effect.

CO_2 Capture and Utilization

Cyclic carbonates from glycols in sc-CO_2

CO_2 pressure and temperature effect



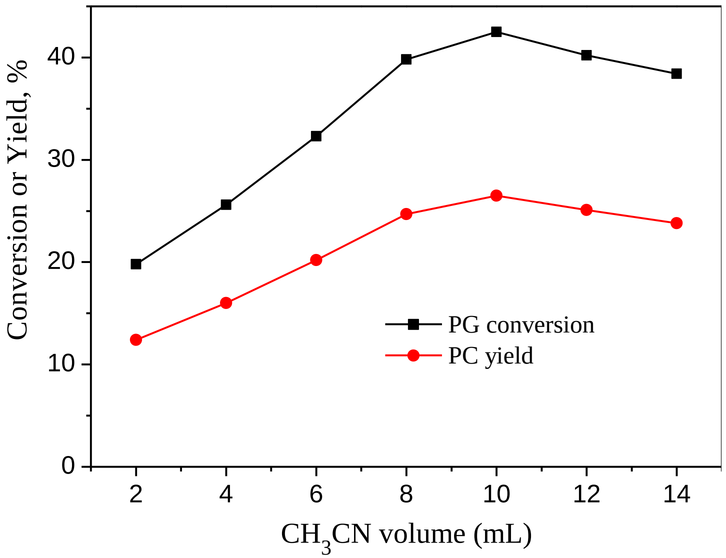


PG conversion and PG yield were highly improved by sc-CO_2 and the optimal pressure was 10MPa in present work.

CO_2 Capture and Utilization

Cyclic carbonates from glycols in sc-CO_2

The effect of CH_3CN on the reaction



Regent	PG Conv. %	PC Yield %
$CaCl_2$	0	0
$MgSO_4$	0	0
4A zeolite	0	0

CH_3CN was very important for the synthesis. CO_2 could be easily dissolved in CH_3CN, and the hydration of CH_3CN led to the removal of H_2O with the optimal mount.

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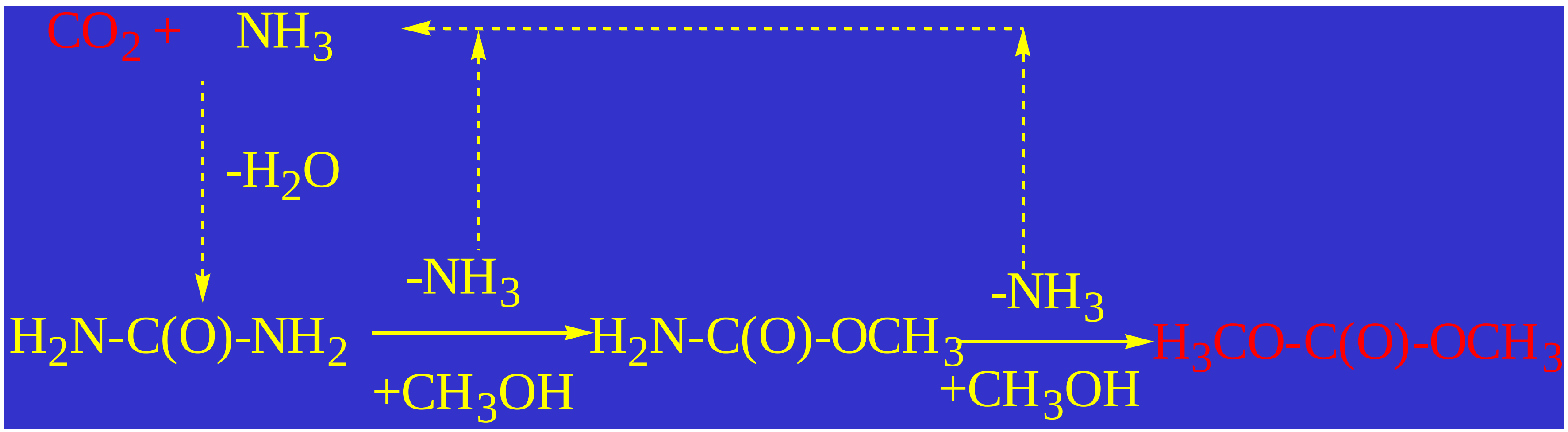
CO_2 Capture and Utilization

Synthesis of DMC from urea and methanol



Urea **Methyl Carbamate(MC)** **DMC**

High DMC yield can be achieved with effective product removal

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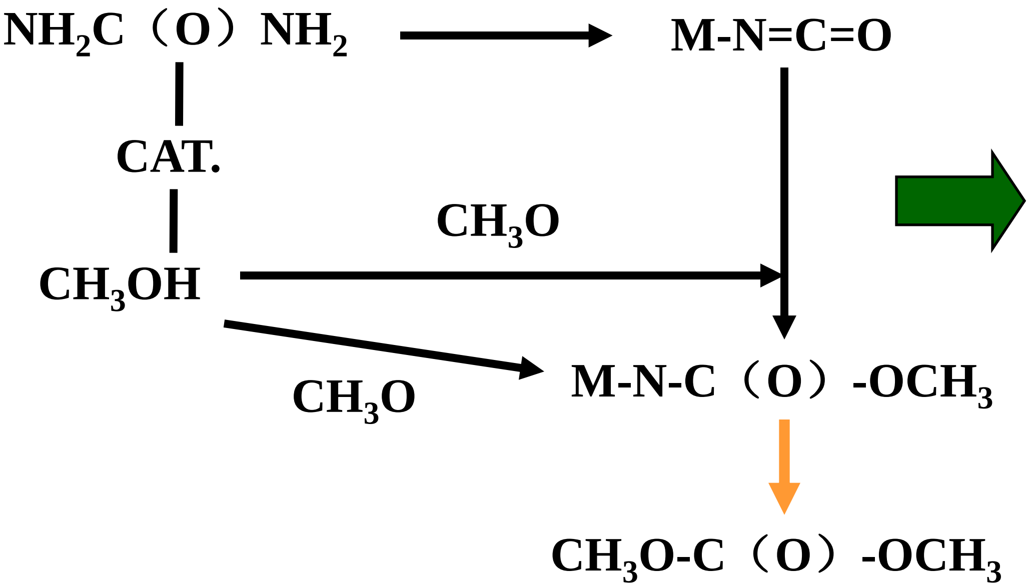
CO_2 Capture and Utilization

Synthesis of DMC from urea and methanol



CATALYST: $M_1X_n/M_2M_3O_x$

M_1= Ni, Co, Zn, Sn, Pb etc

M_2= Zr, Al, La, etc

M_3= Mg, Ca, Ba etc

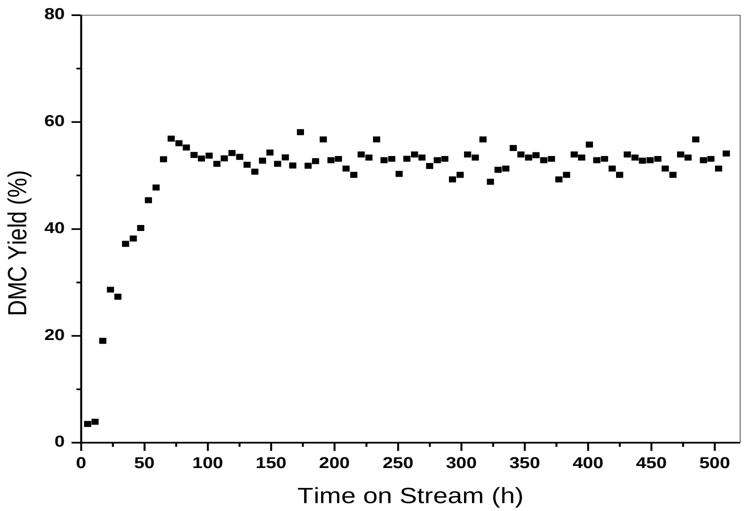
X = Ac, I, NO_3^{2-} etc

Catalyst

The mechanism on solid catalysts

CO_2 Capture and Utilization

Synthesis of DMC from urea and methanol

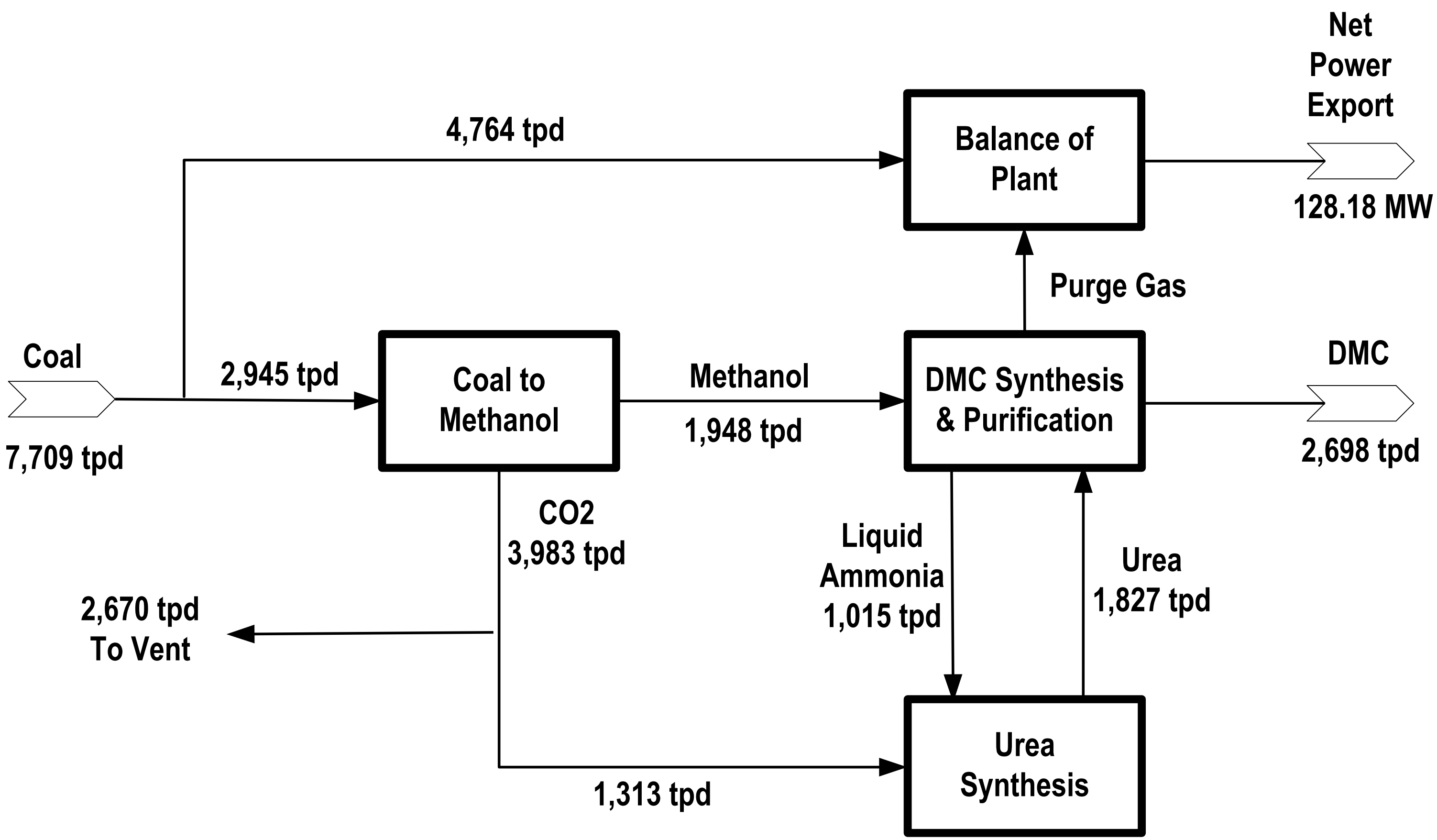


5000t/a Demonstration Plant

The price is about $600/ton on the base of 5000 ton /year demo, which is almost the half price by other technologies.

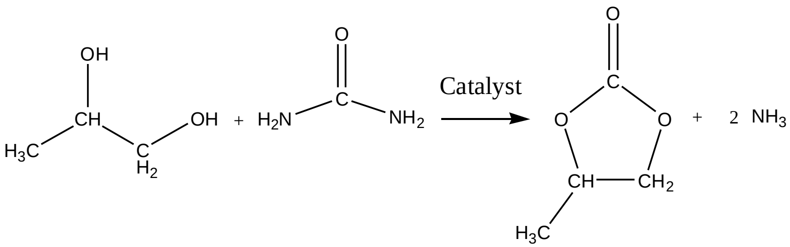
CO_2 Capture and Utilization

Coal Chemical process without CO2 emission

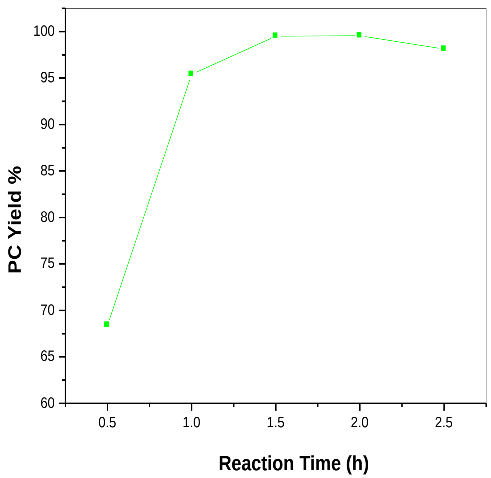


CO_2 Capture and Utilization

Cyclic carbonate from urea and diol



500t/a Demo



entry	diols	alkylene carbonate	Yield (%)
1	1,2-ethanediol	1,2-ethylene carbonate	95.1
2	1,2-propanediol	1,2-propylene carbonate	99.6
3	1,2-butanediol	1,2-butylene carbonate	99.4
4	2,3-butanediol	2,3-butylene carbonate	92.4
5	1,2-cyclohexanediol	1,2-cyclohexylene carbonate	90.5
6	1,3-propanediol	1,3-propylene carbonate	73.
7	1,3-butanediol	1,3-butylene carbonate	74.3

Summary

ICC has developed the solid absorbents and CFB process for in-situ application for flue gas, and led to low cost for CO_2 capture.

ICC has developed some processes for CO_2 chemical utilization.

Acknowledge

MOST

CAS

NSFC

PetroChina

Thanks!